

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Production of Phenols.

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of phenol by the acid-catalyzed cleavage of cumene hydroperoxide wherein the cleavage reaction mixture containing phenol, acetone and the acid cleavage catalyst is neutralized and treated in a phenol-acetone separation means. In particular, this invention relates to an improved method of neutralizing the cleavage reaction mixture.

The manufacture of phenol by partial oxidation of cumene followed by the acid-catalyzed cleavage of the resulting hydroperoxide to form phenol and acetone has been widely accepted in the industry. The cleavage is usually effected in the presence of a mineral acid, for example an aqueous solution of sulfuric, hydrochloric or perchloric acid, and it is necessary to neutralize the cleavage reaction mixture to avoid further reaction during subsequent treatment thereof. Neutralization of the cleavage reaction mixture is conveniently carried out by sorption of the acidic anion on an anion exchange resin. Such an operation suitably removes the anion but it is also accompanied by sorption of a considerable amount of the phenol product on the resin. When the resin is subsequently regenerated by treatment with alkaline solution, the residual phenol sorbed thereon is liberated into the waste alkaline solution in appreciable amounts resulting not only in product loss,

but perhaps more important, in a serious waste disposal problem.

The present invention provides a method of neutralizing the reaction mixture resulting from the acid-catalyzed cleavage of cumene hydroperoxide utilizing an anion exchange resin, which method obviates phenol loss due to caustic regeneration of the spent resin.

Accordingly, the present invention provides a process for the preparation of a phenol by the acid-catalyzed cleavage of a hydroperoxy derivative of a secondary alkyl aromatic hydrocarbon, wherein the cleavage reaction mixture comprising phenol, aliphatic ketone and acid catalyst is neutralized by contacting said mixture with an anion exchange resin, phenol and ketone are recovered from the neutralized reaction mixture, and thereafter the spent anion exchange resin is regenerated by treatment with an alkaline solution, characterized by the improvement which comprises contacting the spent resin before treatment with the alkaline solution with an aliphatic ketone thereby displacing sorbed residual phenol from the spent resin, and recovering the resultant displaced residual phenol.

According to a preferred embodiment of the invention, in producing phenol by the hydrochloric acid-catalyzed cleavage of cumene hydroperoxide in a cleavage reactor, wherein the cleavage reaction mixture comprising phenol, acetone and hydrochloric acid recovered from the cleavage reactor is neutralized and treated in a phenol-acetone separation means, and wherein said cleavage reaction mixture is neutralized by contact with an anion exchange resin, said resin, prior to regeneration thereof by means of an alkaline solution, is contacted with acetone to displace the residual phenol, which

is then recovered. In a still more advantageous embodiment the spent resin before regeneration is treated both with the ketone and with at least a portion of the acid cleavage catalyst. The ketone so utilized preferably is combined with additional cleavage reaction mixture, while acid catalyst so utilized is transferred to the cleavage reactor.

Another feature of this invention is the use of a tertiary amine anion exchange resin. Preferably the spent anion exchange resin, prior to regeneration thereof, is contacted alternately with ketone and with at least a portion of the acid cleavage catalyst in ketone solution, the displaced residual phenol being recovered from solution with said ketone and from said acid catalyst-ketone solution by passing the latter to the cleavage reactor and combining the former with the aforesaid cleavage reaction mixture recovered from the cleavage reactor. Other embodiments and objects of this invention will become apparent in the following detailed description.

As has been stated, the manufacture of phenol through partial oxidation of comene and acid cleavage of the resulting hydroperoxide to form phenol and acetone has been widely accepted in the industry. The process has been applied to the partial oxidation of secondary alkyl aromatic hydrocarbons in general, and particularly to secondary alkyl benzenes, and acid cleavage of the resulting hydroperoxide to yield a corresponding phenol and an aliphatic ketone. Similarly, the process of this invention is applicable to the treatment of cleavage reaction mixtures resulting from the acid-catalyzed cleavage of hydroperoxy derivatives of secondary alkyl aromatic hydrocarbons in general, including cycloalkyl aromatic hydrocarbons such as cyclohexyl benzene, and particularly cleavage reaction mixtures resulting from the acid catalyzed cleavage of α,α -dimethylbenzyl hydroperoxide, more commonly known as cumene hydroperoxide, α -methyl- α -ethylbenzyl hydroperoxide, α,α -dimethyl-*p*-methylbenzyl hydroperoxide, α,α -dimethyl-*p*-ethylbenzyl hydroperoxide, $\alpha,\alpha,\alpha^1,\alpha^1$ -tetramethyl-*p*-xylyl hydroperoxide, α,α -dimethyl-*p*-*t*-butylbenzyl hydroperoxide and α,α -dimethylnaphthylmethyl hydroperoxide.

Neutralization of the cleavage reaction mixture is effected by means of an anion exchange resin, preferably a weakly basic anion exchange resin. A variety of such resins is available. The more common of them contain mixtures of secondary and tertiary amine functional groups. Those containing only tertiary amine functional groups have given the better results. Certain anion exchange resins, for example those based on matrices which are phenol-formaldehyde

condensates or styrene-divinylbenzene copolymers, exhibit high porosity and surface area. These are desirable in that a larger number of readily accessible functional sites per unit weight are available for the neutralization process herein contemplated.

In the neutralization of the cleavage reaction mixture by sorption of the acidic anion on the anion exchange resin, a considerable amount of the phenol product is also sorbed on the resin. The exact relationship between the spent resin and the residual phenol retained thereon has not been ascertained. It may be that the residual phenol is retained on the spent resin in chemical combination therewith as opposed to physical combination. However, it is quite possible that the residual phenol is retained in both chemical and physical combination with the spent anion exchange resin, the amount retained by either means being dependent on the particular anion exchange resin employed.

In the present invention it is preferred that the residual phenol be recovered from the spent anion exchange resin prior to caustic regeneration by contacting the resin with a portion of the aliphatic ketone recovered from the phenol-ketone separation means. The residual phenol is recovered in admixture with the ketone and will usually contain at least a small amount of the acid cleavage catalyst. Phenol loss is avoided by combining this mixture with the cleavage reaction mixture recovered from the cleavage reactor and subsequently neutralized in the manner herein described. Any residual phenol remaining on the spent resin, for example, that retained on the resin by chemical combination therewith, is recovered therefrom by further contacting the spent resin with at least a portion of the acid cleavage catalyst prior to utilization as such in the cleavage reactor. The acid catalyst is preferably utilized in an aliphatic ketone solution to effect a better penetration of the resin. The residual phenol displaced by the acid cleavage catalyst is recovered in admixture therewith and sent to the cleavage reactor together with the catalyst. The aliphatic ketone and the acid cleavage catalyst may be contacted with the spent resin in the described manner in alternate flow one or more times to effect substantially quantitative recovery of the residual phenol.

The process of this invention is preferably effected in a continuous manner. One continuous type of operation is described with reference to the attached schematic flow diagram. The diagram shows three neutralization vessels numbered 1, 2 and 3, each of which contains an anion exchange resin. To effect a continuous type of operation, the said vessels are arranged so that any two consecutive vessels, i.e., 1 and 2, 2 and 3,

or 3 and 1, may be utilized in series to effect neutralization of the cleavage reaction mixture while the remaining vessel is in the process of resin regeneration. For the purpose of the present description vessels 1 and 2 are utilized in one neutralization step and vessel 3 is in the process of regeneration.

A cleavage reactor 4, an acid cleavage catalyst storage vessel 5 and an acetone storage vessel 6 are also shown. The acetone is supplied to the acetone storage vessel through line 21 from a phenol-acetone separation means not shown, for example a fractionation column. The acid cleavage catalyst is maintained in the catalyst storage vessel 5 having been charged thereto through line 9 from an external source.

The present description is with reference to the preparation of phenol. Accordingly, cumene hydroperoxide, resulting from the partial oxidation of cumene, is charged to the cleavage reactor 4 through line 7. The cumene hydroperoxide charge is decomposed in said reactor in the presence of the acid cleavage catalyst introduced to the reactor from the storage vessel 5 by way of line 8. The cleavage reaction mixture comprising phenol, acetone and acid catalyst is withdrawn from the cleavage reactor through an overhead line 10 and passed to neutralization vessel 1 by way of line 11 and open valve 12, (valves 48 and 49 being maintained in a closed position when the neutralization vessels are used in the sequence herein described). The cleavage reaction mixture continues downwardly through vessel 1 in contact with the anion exchange resin contained therein and is withdrawn from said vessel by way of line 13. (Valve 47 located in line 13, valve 30 located in line 27 and valve 32 located in line 35 are in a closed position.) The cleavage reaction mixture then passes through an open valve 15 located in line 14, passing by way of line 14 to line 16 and downwardly in neutralization vessel 2. The cleavage reaction mixture continues downwardly through neutralization vessel 2 in contact with the anion exchange resin contained therein and exits from said vessel through an open valve 19 located in line 17. From line 17, the neutralized cleavage reaction mixture is sent to a phenol-acetone separation means which is not shown, usually a fractionation column. Valve 18 located in line 20 (employed when vessel 2 and 3 are utilized in sequence), valve 33 located in line 36 and valve 29 located in line 26 (utilized when vessel 2 is in the process of regeneration) are in a closed position.

In the course of the neutralization process utilizing vessels 1 and 2 in sequence, the spent anion exchange resin disposed in vessel 3 is subjected to regeneration in the following manner:

Acetone, from the acetone storage vessel 6, is withdrawn therefrom through valve 23 located in line 22 and charged to line 25. At this time, valve 24 in line 25 is in a closed position. The acetone passes by way of line 25 through valve 28 and then upwardly through vessel 3. Valve 30 in line 27 and valve 29 in line 26 (provided for the regeneration process with respect to vessels 1 and 2) are closed. Also, valve 43 located in line 44, and valve 46 located in line 45, and also valve 34 in line 31 are maintained in a closed position during regeneration of the resin in vessel 3. The acetone is passed upwardly in vessel 3 in contact with the spent resin. When the acetone has reached a level in vessel 3 so that substantially all of the spent resin has been contacted, the acetone flow is reversed, the acetone being withdrawn from vessel 3 via line 25 and valve 28. The acetone is returned through line 25 and valve 24 located therein, and combined with the cleavage reaction mixture withdrawn from the cleavage reactor 4 through line 10. In the return acetone flow valve 23 is turned to a closed position. In this manner, the acetone, containing residual phenol from the spent resin and usually at least trace amounts of the acid catalyst, is combined with the cleavage reaction mixture to be treated and recovered therewith in the manner described.

After vessel 3 has been drained of acetone, the spent resin is similarly treated with the acid cleavage catalyst. Accordingly, at least a portion of the acid catalyst is withdrawn from the storage vessel 5 by way of line 31 and charged through valve 34 to vessel 3, valves 28, 43 and 46 being in a closed position during the acid treatment. The acid catalyst charge is continued upwardly in vessel 3 in contact with the spent resin. When substantially all of the resin has been contacted, the acid catalyst flow is reversed and the acid catalyst is returned to the cleavage acid storage vessel by the same route as charged. As previously mentioned, the acid catalyst is preferably utilized in acetone solution to effect a better penetration of the resin, in which case acetone from the acetone storage vessel 6 may be admitted to the said catalyst stream through line 25 and valve 28 during the acid treatment of the resin. The spent resin may be alternately treated with acetone and acid catalyst one or more times prior to caustic regeneration hereinafter described.

Subsequent to the acetone and acid treatment, the spent resin is water-washed and thereafter treated with alkaline solution. Water for the water-wash step is charged through line 37 and passes upwardly through vessel 3. The water flow continues upwardly through the resin bed being withdrawn through line 38 and discharged to

waste. Lines 39 and 40 of vessel 2, and lines 41 and 42 of vessel 1, correspond to lines 37 and 38 of vessel 3 and are similarly utilized in the regeneration process.

- 5 Regeneration of the spent resin is effected by charging the alkaline solution through line 37 to vessel 3 in the same manner as the previously described water-wash and similarly discharged to waste through line 10 38. The regeneration treatment is followed by a water-wash in the described manner prior to re-utilization of the regenerated resin in the neutralization process.

- 15 Also included in the schematic flow diagram are a number of lines and valves which are not utilized in this particular flow description but necessary to effect a continuous process wherein the neutralization vessels are periodically alternated between 20 the neutralization step and the regeneration step as herein contemplated.

The following examples are presented in further illustration of the process of this invention.

25 EXAMPLE I

- A weakly basic anion exchange resin known under the trade mark "Amberlyst A-21" and containing tertiary amine functional groups was placed in a vertical 30 column of 50 cc. capacity. The resin bed had a final expanded volume of 10 cc. A cleavage reaction mixture comprising about 46% phenol, 34% acetone, 20% cumene, and also including 0.15% HCl and 1.1% water, 35 was processed downflow through the resin bed at a rate of 40 cc. per hour. In all, 550 grams of the cleavage reaction mixture was processed through the resin bed.

- 40 Thereafter, acetone was charged upflow through the resin bed until the bed was immersed therein. After a period of about 30 minutes, the acetone was drained into a receiver. Following the acetone treatment the resin bed was similarly treated with a solu- 45 tion consisting of 6% HCl, 54% water and 40% acetone, the solution being drained into a receiver after a period of about 30 minutes. The phenol elimination washes were followed by similar treatment of the resin 50 bed with aqueous 2N sodium hydroxide solution. In each case, the washings were collected in a receiver and analyzed for phenol by ultraviolet spectroscopic methods. The results of this treatment are tabulated 55 below.

Wash Number	Phenol Recovery (gms)
1-(acetone)	3.90
2-(acetone-HCl)05
60 3-(acetone)18
4-(acetone-HCl)02
5-(acetone)19
6-(acetone-HCl)02
7-(acetone)20
65 8-(sodium hydroxide)	0.06

EXAMPLE II

In this example, a weakly basic anion exchange resin known under the trade mark "Duolite A-7" and containing both secondary and tertiary amine functional groups 70 was substituted for the anion exchange resin of Example I. The resin was treated with a cleavage reaction mixture, alternately treated with acetone and hydrochloric acid 75 in acetone solution, and finally with a caustic solution, all in the same manner and under the same conditions as Example I. The results are tabulated below;

Wash Number	Phenol Recovery (gms)	
1-(acetone)	2.40	
2-(acetone-HCl)	0.25	
3-(acetone)	0.17	
4-(acetone-HCl)	0.08	85
5-(acetone)	0.08	
6-(acetone-HCl)	0.04	
7-(acetone)	0.04	
8-(sodium hydroxide)	0.17	
Total	3.23	90

As will be observed, the sodium hydroxide wash is in each case very low in phenol content. Phenol in the acetone and in the acetone-hydrochloric acid wash is recycled 95 through the neutralization process, as illustrated with reference to the schematic flow diagram, and subsequently recovered. Recovery in Example I was 98.8% and in Example 2, 94.8%. The process of the invention thus enables maximum phenol recovery 100 by obviating phenol loss to the alkaline solution utilized in regeneration of the spent ion exchange resin. The process also minimizes the disposal problem which results from the 105 presence of sodium phenylates in the waste water.

We are aware of Patent Specification No. 970,945 in the name of Societa Italiana Resine.

WHAT WE CLAIM IS:—

- 110 1. A process for the preparation of a phenol by the acid-catalyzed cleavage of a hydroperoxy derivative of a secondary alkyl aromatic hydrocarbon, wherein the cleavage reaction mixture comprising phenol, ali- 115 phatic ketone and acid catalyst is neutralized by contacting said mixture with an anion exchange resin, phenol and ketone are recovered from the neutralized reaction mixture, and thereafter the spent anion exchange 120 resin is regenerated by treatment with an alkaline solution, characterized by the improvement which comprises contacting the spent resin before treatment with the alkaline solution with an aliphatic ketone thereby 125 displacing sorbed residual phenol from the

spent resin, and recovering the resultant displaced residual phenol.

2. Process according to claim 1, further characterized in that the spent anion exchange resin, prior to regeneration thereof, is contacted with an aliphatic ketone and with at least a portion of the acid cleavage catalyst and displaced residual phenol is recovered in admixture with said ketone and in admixture with said acid catalyst.

3. Process according to claim 1 or 2, further characterized in that the spent resin is contacted with an aliphatic ketone containing acid cleavage catalyst.

4. Process according to claim 2, further characterized in that the spent resin is contacted alternately with the aliphatic ketone and with the acid cleavage catalyst, resulting mixture of phenol and acid catalyst is returned to the cleavage reaction and resulting mixture of phenol and aliphatic ketone is combined with cleavage reaction mixture.

5. Process according to claim 4, further characterized in that the spent resin is contacted alternately with the aliphatic ketone and with a solution of the acid cleavage catalyst in the aliphatic ketone.

6. Process according to any of the claims 1 to 5, further characterized in that the hydroperoxy derivative of a secondary alkyl

aromatic hydrocarbon is a hydroperoxy derivative of a secondary alkyl benzene.

7. Process according to any of the claims 1 to 6, further characterized in that the spent resin is contacted with an aliphatic ketone which is the same as that contained in the cleavage reaction mixture.

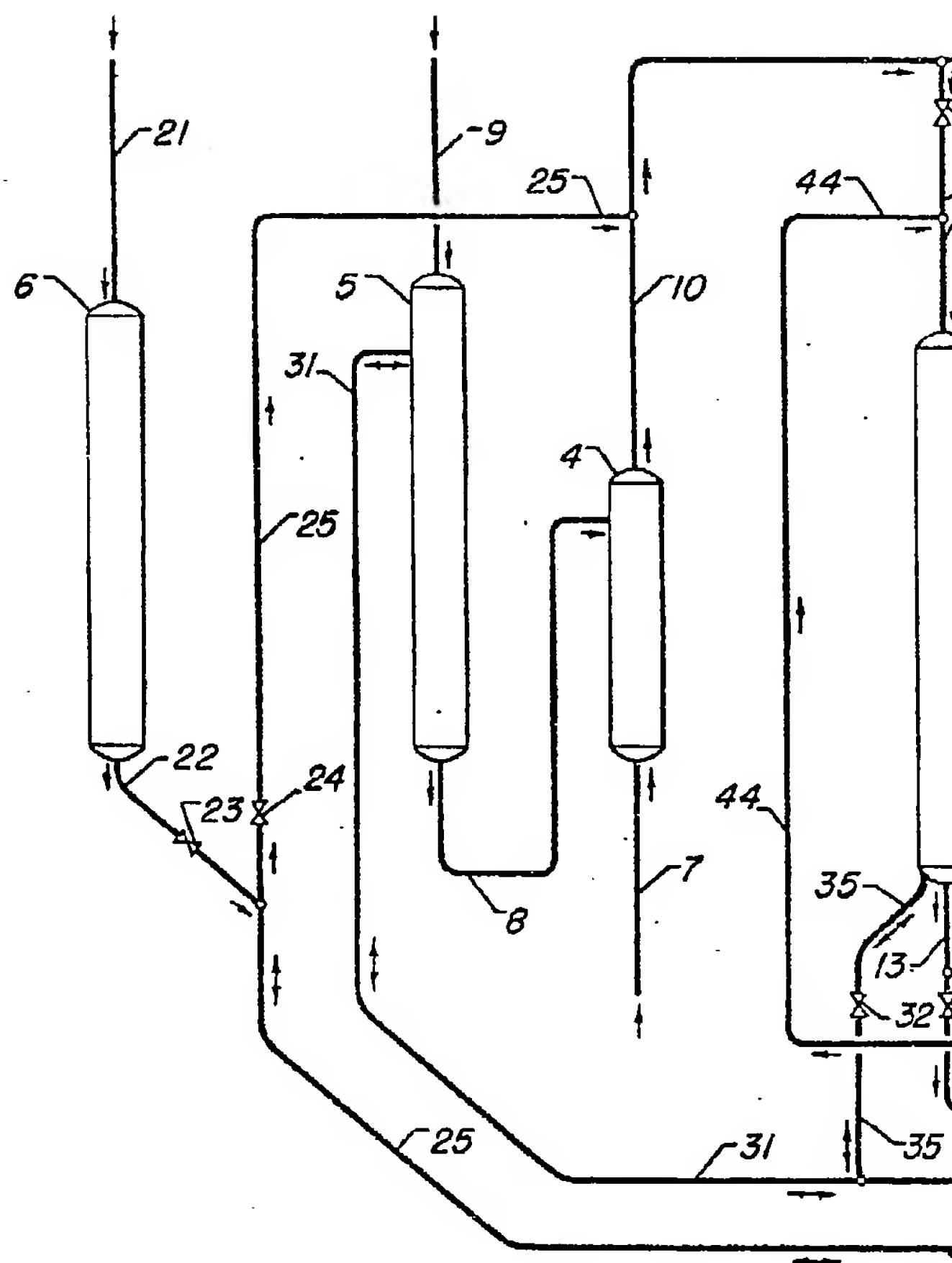
8. Process according to claim 6, further characterized in that phenol is produced by the acid-catalyzed cleavage of cumene hydroperoxide, the cleavage reaction mixture contains phenol, acetone and acid catalyst, and the spent anion exchange resin is contacted with acetone before treatment with the alkaline regeneration solution.

9. Process according to any of the claims 1 to 8, further characterized in that the acid cleavage catalyst is sulfuric, hydrochloric or perchloric acid.

10. Process for the preparation of a phenol as claimed in claim 1 and substantially as hereinbefore described.

J. Y. & G. W. JOHNSON,
Furnival House,
14-18, High Holborn,
London, W.C.1.
Chartered Patent Agents,
Agents for the Applicants.

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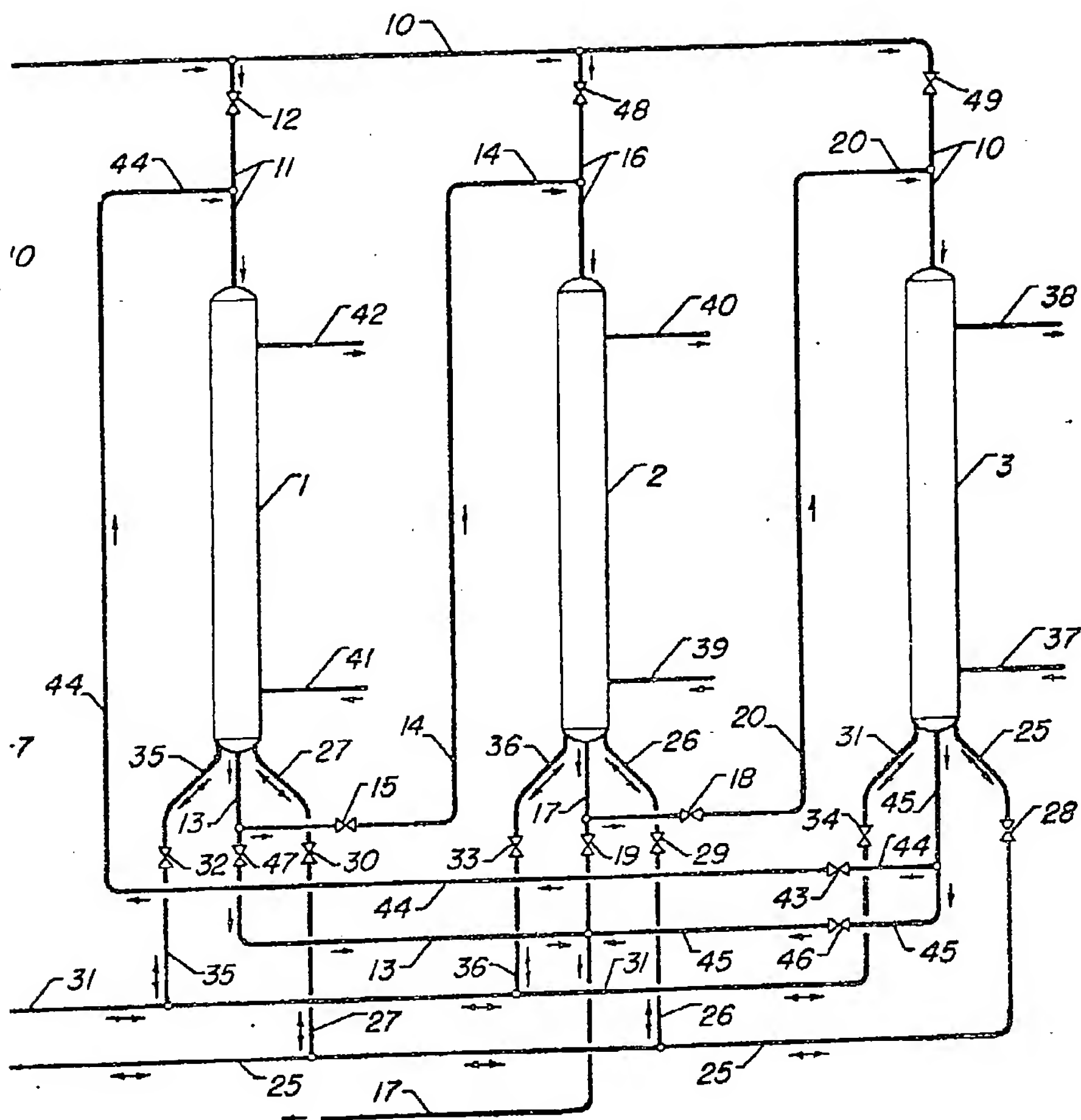


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